

Methanolysis of microbial polyester poly(3-hydroxybutyrate) catalyzed by Brønsted-Lewis acidic ionic liquids as a new method towards sustainable development



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ABSTRACT

Chemical recycling of bio-based polymer poly(3-hydroxybutyrate) (PHB) by methanolysis was discussed in detail from the perspective of biological refining. The results of methanolysis transformed PHB into ester monomer successfully by using some ionic liquids. PHB was depolymerized into methyl 3-hydroxybutyrate (M3HB) at lower degradation temperatures in the presence of Brønsted-Lewis acidic ionic liquid 1-(3-sulfonic acid)-propyl-3-methylimidazole ferric chloride ([MIMPS]FeCl₄) as catalyst. Obtained M3HB from this reaction can be used in many areas, which is consistent with the principles of sustainable development. Then, the influences of reaction parameters on PHB methanolysis were investigated and the optimum conditions were obtained. Under the optimum conditions, the conversion of PHB and yield of M3HB was 98.5% and 87.4%, respectively. This catalyst could be recycled up to 6 times with no apparent decrease in catalytic activity. At the same time, the methanolysis mechanism of PHB is proposed through the experiments. In addition, kinetic study indicated that this reaction was pseudo-first-order reaction with activation energy of 24.74 kJ/mol.

1. Introduction

Currently, the global production of chemical synthetic plastics has more than hundreds of millions of tons every year, most of them are difficult to be degraded in nature, which can result in an increasingly serious environmental pollution problem [1]. Poly(3-hydroxybutyrate) (PHB), as a microbial synthetic plastics, it has many similar performances with polypropylene (PP) and polystyrene (PS) under room temperature condition, such as similar glass temperature, melting point, and degree of crystallinity [2–4]. As a kind of polymer materials derived from microbial synthesis, PHB has some advantages such as good optical activity, biodegradability and biocompatibility, so it is expected to be widely used in the fields of textile, food packages [5–7], tissue engineering [8], biomedical and many other high-tech fields [9–12]. With the decreasing of PHB production costs, the increasing of production and consumption, the amount of waste PHB will be more and more. Although PHB can be biodegraded into non-toxic and harmless products in the natural environment, its degradation rate is related to various factors such as the environment humidity, temperature and pH value, at the same time also has an intrinsic relationship

with the sample components, crystallinity and surface. Hence, its degradation period is much longer [13,14]. However, chemical methods of recycling waste PHB material, these not only can reduce the amount of solid waste, but also can recover high value-added monomer to prepare other polymers, which is consistent with the requirements of sustainable development. Hence, the recycling technology of PHB has been aroused more and more attention [15–17].

Various methods of chemical recycling of PHB, such as thermal pyrolysis [18–21], hydrolysis [22–24], and photo-degradation [25,26] have been widely put forward in many previous reports. For pyrolysis, the degradation temperatures generally ranged from 170 °C to 300 °C, the final products were crotonic acid (CA) and well-defined oligomers and cyclic oligomers [20,21]. Compared with thermal pyrolysis, hydrolysis does not require higher temperatures, but the products of hydrolysis reactions were mainly some organic acids, which were very difficult to be separated from the reaction mixture. These reactions also used a large amount of traditional inorganic acids or alkalis as catalysts, and these catalysts cannot be reused [22,24]. Although photo-degradation can take place without those catalysts under moderate conditions, its reaction period is too long. Some reactions cannot be

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degraded completely, even if it takes 6 weeks, and did not obtain the useful products [25]. Among these reported methods, alcoholysis is a more important method [27–29], by the transesterification reaction between PHB and alcohols, the corresponding product alkyl esters can be obtained. However, in those previous methods, some different by-products have also been obtained [29], meanwhile the reaction also required lots of strong acids or alkalis as catalysts, and these catalysts need neutralization and washing operations, which would result in equipment corrosion and environmental pollution [27]. In addition, due to the insolubility of PHB in alcohol under atmospheric pressure, this reaction needs to be carried out at high temperature and/or high pressure [26]. Therefore, in order to overcome these above weaknesses, it is very necessary to develop a new catalyst in this reaction.

Ionic liquids (ILs), as an environment-friendly green solvent or catalyst, which have attracted much more attention on their unique property, such as non-volatile, low flammability, excellent thermal stability, good solubility and electrochemical stability, have been used in separation, synthesis, electrochemistry and catalysis [30–33]. Since 2000, ILs have been successfully used in some chemical degradation of polymers, such as polycarbonate [34], poly(ethylene terephthalate) [35,36] and polyamide [37]. Recently, metal halide or acetate-containing ILs, a new kind of Lewis acidic ILs, as promising catalysts, have been received broad attention of scholars in the glycolysis of PET. Wang et al. [38] and Yue et al. [39] used Fe/Zn-containing magnetic ILs [Bmim]FeCl₄/[Bmim]ZnCl₃ in the PET glycolysis, which showed higher catalytic activity than the traditional ILs. Cu- and Zn-acetate-containing (Cu(OAc)₂[Bmim][OAc]), (Zn(OAc)₂[Bmim][OAc]) ILs were also reported to be effective in this reaction [40]. In our previous work, Brønsted acidic IL [MIMPS][HSO₄] had exhibited good catalytic activity in the methanolysis of PLA and PHB [41,42]. Brønsted-Lewis acidic ILs combine the characters of Brønsted-Lewis solid acids and ionic liquids, due to the presence of Brønsted- and Lewis-acidic sites, these ILs can selectively catalyze different reaction mechanisms to enhance the conversion and selectivity, which caused our interesting. To the best of our knowledge, the use of Brønsted-Lewis acidic ILs for the methanolysis of PHB to M3HB has not been reported.

In this work, we present our attempts to synthesize a series of Brønsted-Lewis acidic ILs used to catalyze the PHB methanolysis. And the results showed that Brønsted-Lewis acidic ILs can catalyze efficiently this reaction to obtain M3HB. In addition, the catalysts not only can be recovered by simple separation, but also can be reused. Therefore, this contribution fully illustrates our study of this main objective.

2. Experimental section

2.1. Materials

Virgin pellets of PHB (3.0 mm × 2.8 mm × 3.0 mm) were obtained from Ningbo Tianan biological material Co. Ltd., China. The weight-average molecular weight, number-average molecular weight and PDI of it were 430,000 g mol⁻¹, 204,000 g mol⁻¹ and 2.11, respectively, which were measured by GPC (Waters-515) in chloroform solution at 25 °C. *N*-methylimidazole (MIM), 1,3-propane sultone (PS) and anhydrous ferric chloride (FeCl₃) were purchased from Shanghai McLean

Biochemical Science and Technology Co. Ltd., China. Methanol was purchased from Sinopharm Chemical Reagent Beijing Co., China. Other chemicals (AR) were obtained from Sigma-Aldrich. All these reagents were used without any further purification.

2.2. Preparation of catalysts

2.2.1. Synthesis of 1-(3-sulfonic acid) propyl-3-methylimidazole hydrochloride ([MIMPS]Cl)

The synthesis of IL [MIMPS]Cl was similar to that was used in the previous report [41], and the detailed procedure is as follows.

An amount of 1,3-propane sultone (PS) and ethyl acetate were added into a three-necked flask, which were stirred vigorously to be homogeneous solution at room temperature, then equimolar amounts of *N*-methylimidazole was added dropwise slowly. After dropping, the mixture was heated to 50–55 °C for 2 h. The obtained white solid was washed three times with ethyl acetate, and dried under vacuum at 100 °C for 2 h to obtain the white power [MIMPS] with the yield of 98%. The structure of [MIMPS] was verified by and FT-IR spectroscopy.

¹H NMR (Fig. S1(1), 500 MHz, D₂O, ppm): 2.11 (m, 2H), 2.71 (t, 2H), 3.71 (s, 3H), 4.16 (t, 2H), 7.25 (s, 1H), 7.32 (s, 1H), 8.53 (s, 1H).

IR (Fig. S1(2), KBr film): 3175 (ν, C-H of imidazole ring), 2970, 2880 (ν, -CH₂*-CH₃*), 3437 (ν, -SO₃H*), 1620 (ν, -C=N and -C=C of imidazole ring), 1480, 1150 (β, C-H), 1230–1172 (ν_{as}, -SOH₃*), 853 (γ, -CH₂*-CH₃*), 748 (γ, C-H of imidazole ring).

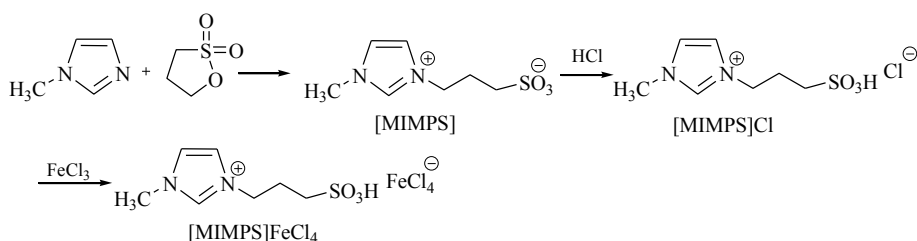
The obtained IL precursor [MIMPS] was dissolved into an amount of distilled water, an equimolar amount of hydrochloric acid (HCl) was dropped at room temperature. After completion of dropping, the reaction temperature was raised to 90 °C rapidly, and the mixture was refluxed for 2 h under stirring. After removing the water of the mixture by vacuum distillation, and dried under vacuum (120 °C, 10 mmHg) for 4 h, the light yellow viscous IL [MIMPS]Cl was produced with the yield of 96.3%.

2.2.2. Synthesis of 1-(3-sulfonic acid)-propyl-3-methylimidazole ferric chloride [MIMPS]FeCl₄

Under the nitrogen atmosphere, equimolar amounts of [MIMPS]Cl and metal chloride (FeCl₃, ZnCl₂ and MnCl₂) were stirred for 8–24 h at room temperature in dichloromethane, after the reaction was completed, the dichloromethane was removed by using a vacuum rotary evaporator. Then, the product was dried for 10 h at 100 °C in a vacuum oven and the IL [MIMPS]FeCl₄ was obtained (Scheme 1).

2.3. General procedures for the PHB methanolysis

A 50 mL autoclave equipped with a magnetic stirrer and a thermometer was loaded with PHB (*w*₀), a certain amount of catalyst and methanol. Under stirring, the methanolysis reaction was performed in the reaction temperature range of 110–150 °C for a methanolysis time of 1–4 h at autogenous pressure. The autoclave was immersed in an oil bath at a given temperature for the prescribed time. When the methanolysis reaction was finished, the mixture was cooled to room temperature rapidly. The undepolymerized PHB pellets were separated from the mixture by filtration, and washed by some amount of methanol, and collected, dried, and weighed (*w*₁). The conversion of PHB



Scheme 1. Synthesis of Ionic Liquid [MIMPS]FeCl₄.

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